Reduction of Hexavalent Chromium by Polypyrrole – Modified Aluminium or Titanium Electrodes

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Chromium has the ability to form stable complexes in a range of oxidation states from -2 to 6. Of these Cr (III) and Cr (VI) are the most common. The latter is generated in a number of processes such as leather tanning and chrome plating. However, hexavalent chromium poses a series risk to the environment, it is toxic, carcinogenic and extremely mobile [1]. However, the trivalent state is less toxic and can be easily absorbed on to a variety of inorganic and organic materials at neutral pH [2] in contrast to the hexavalent form, which is only weakly absorbed onto inorganic surfaces [3]. Thus the conversion of Cr (VI) to Cr (III) is an important step in pollution control. Currently there are a variety of methods been investigated for dichromate reduction which range from biological [4] to physical [5] to chemical. Another possible route is to use conducting polymers to reduce hexavalent chromium.

The first report of the reduction of hexavalent chromium at a conducting polymer matrix was made in 1993 by Rajeshwar and co-workers [6] who observed the reduction of hexavalent chromium at a polypyrrole electrode, with approximately 100% efficiency, and at time intervals spanning only minutes. Polypyrrole (PPy) is a well-known conducting polymer and can undergo good reversibility between its conducting and insulating states [7] as shown in Figure 1.

Fig. 1. Neutral (insulating) and oxidized redox states of polypyrrole.

In this paper a polypyrrole coated aluminium or titanium substrate is employed as an electrocatalyst for the reduction of hexavalent chromium to the less toxic trivalent state in accordance with scheme 1 by synthesising PPy in its positive oxidation state and then reducing it to its neutral insulating state by subjecting it to a negative potential.

$$Cr_{2}O_{7}^{^{2-}}{}_{(aq)} + 14H^{^{+}}{}_{(aq)} + 6PPy^{0} \underset{(s)}{\longleftrightarrow} 2Cr^{^{3+}}{}_{(aq)} + 6PPy^{^{+}}{}_{(s)} + 7H_{2}O_{(l)}$$

Scheme 1

In scheme 1, PPy⁰ and PPy⁺ represent the reduced and

oxidized redox states of the polymer respectively. The PPy films were grown potentiostatically at 1.25 V (SCE) on aluminium or titanium electrodes from aqueous solutions containing 0.3 M pyrrole and 0.1 M tosylic acid. After reduction treatment in a particular electrolyte the films were then washed and transferred to 75 cm³ Cr (VI) (acidified) solution of appropriate concentration for time intervals of 22 hr. The reaction was monitored under open-circuit conditions and samples were withdrawn at regular intervals and subjected to kinetic analysis. The reduction reaction was found to obey pseudo first order kinetics with respect to dichromate. The efficiency of dichromate reduction was found to depend on the electrolyte in which the polymer film was reduced. Polymer degradation occurred after long periods of exposure to dichromate. The influence of the underlying substrate was found to be minimal.

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Acknowledgments

The authors gratefully acknowledge the support of this work by *Enterprise Ireland* and K.G. Conroy would like to gratefully acknowledge the scholastic funding received from *The Scholarships Board* at the National University of Ireland, Maynooth.